Glide matching with binary and ternary zeotropic* refrigerant mixtures Part 1. An experimental study

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An improvement of the coefficient of performance (COP) of the refrigeration cycle can be realized when temperature profiles of the refrigerant mixture and the heat transfer fluid (HTF) are matched. For the same temperature lift, the benefit of glide matching increases as the application glide increases. High-glide binary mixtures composed of components far apart in boiling points tend to have a non-linear relationship between temperature and enthalpy in the two-phase region. The introduction of an intermediate boiler as a third component can linearize this relationship and, theoretically, increase the cycle COP when heat-source and heat-sink fluids are substantially linear (e.g. water, brines, dry air). The research described in this paper was directed at exemplifying this characteristic of ternary mixtures by experimental evaluation of the performance of an R23/142b binary mixture and an R23/22/142b ternary mixture in a generic laboratory breadboard refrigeration system.

(Keywords: zeotropic mixtures; Lorenz cycle; refrigeration; heat pumping; refrigerant mixtures; non-linearity)

Correspondances de glissement avec les mélanges frigorigènes zéotropes binaires et ternaires 1ère partie: Etude expérimentale

On peut améliorer le coefficient de performance (COP) du cycle frigorifique quand les profils des températures du mélange frigorigène et du fluide caloporteur (HTF) sont identiques. Pour le même relevage de température, les correspondances de glissement augmentent parallèlement au glissement lui-même. Le rapport entre température et enthalpie dans les zones biphasiques serait plutôt non-linéaire pour les mélanges binaires très glissants, formés de composants dont les points d'ébullition sont très éloignés. L'introduction d'un générateur intermédiaire comme troisième composant peut linéariser ce rapport et, en théorie, augmenter le COP du cycle quand les fluides sources de chaleur et sources de froit sont très linéaires (par ex., l'eau, les liquides à bas point de congélation, l'air sec). Les recherches décrites dans cet article ont servi à illustrer cette caractéristique des mélanges ternaires en évaluant la performance du mélange binaire R23/142b et du mélange ternaire R23/22/142b dans un système frigorifique expérimental.

(Mots clés: mélanges zéotropes; cycle Lorenz; froid; pompe à chaleur; mélanges frigorigènes; non-linéarité

In theory, the use of zeotropic mixtures can result in an improvement in the cycle coefficient of performance (COP) when the temperature profile of the evaporating and condensing mixture matches that of heat-source and heat-sink fluids in the counter-flow evaporator and condenser. The benefits are derived from reducing the irreversibilities in the heat exchangers.

The concept of glide matching is presented in Figure 1 where Carnot and Lorenz cycles are shown working at the same temperature profiles of the heat transfer fluid (HTF). The shaded areas in the figure are approximations of the heat transfer irreversibilities. For the Carnot cycle, even infinite heat exchangers cannot eliminate the irreversibilities if a sensible HTF is used, as is shown in the figure. However, for the Lorenz cycle, increase in the heat transfer area will cause decrease in heat transfer irreversibilities. (Note that the temperature profile of the HTF is shown in Figure 1 to provide a reference for outlining the two thermodynamic cycles, and not to indicate HTF's entropy change in the evaporator and condenser; transfer of heat at a finite temperature difference causes unequal entropy changes of the heatexchanging fluids.)

Sensible fluids such as water, brines and air without condensation occurring exhibit nearly constant specific heats over the temperature range experienced in the heat exchanger, which results in a nearly linear temperature profile during heat exchange. Unfortunately, the temperature of high-glide zerotropic mixtures generally does not change linearly as a function of enthalpy (or of entropy, which is nearly the same physical requirement). This results in non-linear refrigerant profiles with the potential to 'pinch' with the sensible fluid, as illustrated in Figure 2.

0140-7007/94/040220-06

^{*} The word 'zeotropic' is used to describe a refrigerant mixture which changes (tropic) in boiling (zeo) behaviour, in lieu of the double negative prefixed non-azeotropic.

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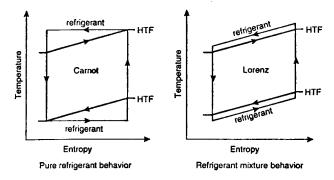


Figure 1 Efficiency advantage of the Lorenz cycle

Figure 1 Rendement du cycle Lorenz

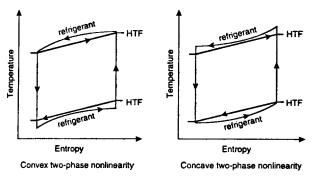


Figure 2 Inefficiencies resulting from two-phase non-linearity
Figure 2 Inefficacité due à la non-linéarité biphasique

An approach to visualize the correcting of this two-phase non-linearity via third component is shown in Figure 3. Here, each component of a mixture is shown as an area of height equal to its boiling point and of length equal to its total enthalpy (mass fraction times specific enthalpy). The top figure represents a binary where the predominant thermal component is the more volatile one (i.e. lower boiling point). This results in a concave profile because considerable evaporation must occur before the influence of the less volatile component is felt.

The middle figure represents the opposite case where the less volatile component is felt rather early in the evaporation process and so the binary's saturation temperature begins changing significantly at very low qualities and convex profiles result. We conjectured that by adding a fluid of intermediate boiling point, the temperature profile might be linearized. It is this concept this study attempted to verify, and so the binary and ternary components and compositions were selected purely on the basis of their normal boiling points. The magnitude and non-linearity of the temperature glide will tend to increase as the extreme components are selected with more widely diverging boiling points. Introduction of a fluid with an intermediate boiling temperature will tend to even out the rate of change of the temperatureenthalpy curve.

Test apparatus and test procedure

The tests were conducted on a breadboard heat pump apparatus which was constructed for a previous study and is described in detail in reference 1. In essence, the system works as a counter-flow, water-to-water heat pump.

The evaporator was composed of two 6.1 m (20 ft) sections, each bent into a hairpin shape for compactness, connected in series. The sections are extrusions with an integrally finned centre passage surrounded by rectangular passages. In the tested configuration, evaporating refrigerant flowed through the centre passages and heat source water through the surrounding rectangular passages. Hard copper tubes were attached over the four hairpin legs to create a third concentric passage used (in some of the tests) for heat exchange between refrigerant leaving the condenser and the heat source water throughout the length of the evaporator. Thermocouples were spaced at 2 ft (0.61 m) intervals inside 10 ft (3.05 m) long wells which were inserted into the evaporating refrigerant centre passages of each hairpin leg. The heat-source water temperature was measured in wells at the inlet and outlet, and by surface thermocouples at the cross-over between each 10 ft section. Temperature profiles measured by these thermocouples are presented in *Figure* 6.

The system employed a positive displacement, suction-vapour-cooled, open compressor driven by a variable-speed motor through a shaft dynamometer. The expansion device was operated manually. The design of the condenser did not allow placing thermocouples inside the heat exchanger; only inlet and outlet refrigerant and HTF temperatures were measured.

The evaporator capacity was measured by a calorimeter method with the enthalpy method on the evaporator—water side as a secondary measurement. The water flow was measured by a turbine meter and by comparing the temperature change of the water across the metered electric heaters used to load the evaporator. Analogous methods to the secondary evaporator capacity measurement methods were applied to the condensing water loop to measure the condenser capacity.

All tests were performed with evaporator water entering and leaving temperatures of 26.7 °C (80 °F) and 12.8 °C (55 °F), respectively, and condenser entering and leaving water temperatures of 27.8 °C (82 °F) and 47.2 °C (117 °F).

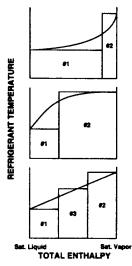


Figure 3 Conceptual view of mixture temperature non-linearity
Figure 3 Schématisation de la non-linearité des températures des mélanges

The evaporator exit close-to-saturation condition was maintained by two accumulators installed in series. A conventional accumulator with an oil return J tube was located directly in front of the compressor and was used to protect the compressor on start-up. This accumulator was valved off and bypassed during steady-state operation at which time it would store excess refrigerant in the system. Another accumulator was located at the evaporator outlet and was used to establish a consistent state of slightly misty vapour leaving the evaporator as a test criterion and to reduce sensitivity to refrigerant charge. This system design ensured that only vapour with a slight mist carry-over could leave, establishing the evaporator exit condition as near saturation.

Subcooling was controlled with a manually operated expansion valve. In previous tests on this apparatus. subcooling was adjusted to be as near saturation as possible but still subcooled1. This criterion was somewhat unfair to pure refrigerants and to undergliding zeotropic mixtures. Their COP can be increased by subcooling to as near the inlet water temperature as possible without pinching. Therefore, this series of tests was performed with two subcooling criteria: first, that the liquid line sight glass was clear; and, second, that the temperature of the refrigerant leaving the condenser was near that of the inlet water (27.8 °C (82 °F)). In practice this temperature ranged from 28 °C (82.4 °F) to 33.1 °C (91.5°F). Exceptions to this criterion were several tests in which the effect of heat transfer between the liquid line and the evaporator was studied; in these tests, in which the refrigerant appeared to be non-linearly pinching at the condenser outlet, the expansion valve was opened to allow two-phase refrigerant leaving the condenser.

Because the coefficient of performance of vapour compression systems is sensitive to heat exchanger size per unit capacity, and the heat exchanger size was fixed, it was desired to run tests at constant evaporator capacity using the variable-speed compressor drive to compensate for the variations in capacity inherent in the different refrigerants to be tested. This criterion was compromised by the need to avoid the 600-800 rev min⁻¹ band in which high system vibrations and unduly reduced efficiency were observed. In practice, measured evaporator capacities range from $3.119 \, kW \, (10730 \, Btu \, h^{-1})$ to $4.457 \, kW \, (15330 \, Btu \, h^{-1})$ with the exception of test 21, which was performed at $5.777 \,\mathrm{kW}$ (19870 Btu h⁻¹). The very large size of the heat exchangers (resulting in approximately 2.8 °C (5 °F) average effective temperature difference and R22 pinching at approximately 1/4 the evaporator length) somewhat reduced sensitivity to this heat exchanger size criterion.

Refrigerant composition was determined by gas chromatographic analysis of samples taken from the compressor discharge line at the beginning and end of each test. The composition would change from test to test for the same initial charge as a result of differing amounts of refrigerant being held in the separating accumulator at the evaporator outlet, which would selectively store the less volatile mixture components.

Test plan

The binary mixture chosen for this study was one of R23 (trifluoromethane) and R142b (chlorodifluoroethane). These refrigerants are quite far apart in their normal boiling points, $82.1 \,^{\circ}\text{C}$ (-115.7 $^{\circ}\text{F}$) and $-9.8 \,^{\circ}\text{C}$

(14.4°F), respectively, suggesting that their mixture would tend to have a high temperature glide and a significant temperature-enthalpy or temperatureentropy non-linearity in the two-phase region. The intermediate boiler chosen for demonstration of linearization by addition of a third component was R22 (chlorodifluoromethane) characterized by a normal boiling point of -40.8 °C (-41.4 °F).

The tests were planned to indicate the best-performing compositions of the R23/142b and R23/22/142b mixtures with the constraint not to exceed the operating pressure of R22. The best COP was expected to occur near the point of glide matching to the heat-source fluid, i.e. at a 13.9 °C (25 °F) glide. For the binary mixture, the best performance could be found by stepping the composition from one pure component to the other in equal intervals with extra points taken in areas of rapid performance change and near efficiency peaks. The extra degree of freedom provided by ternary mixtures required more thought as to appropriate test compositions.

A two-phase temperature glide diagram for the studied ternary, R23/22/142b, proved to be helpful in planning the experiment. Such a diagram is shown in Figure 4, where the temperature glide for the mixture is mapped in 21 mass-fraction steps with +/- non-linearities noted parenthetically and R22 isobar superimposed². The positive and negative non-linearity numbers indicate the maximum and minimum that the mixture temperature exceeds that of a hypothetical linear fluid (i.e. ideal mixture) on a temperature-enthalpy diagram, where both fluids are compared at the same quality point and have the same bubble and dew point properties. The R22 isobar indicates those compositions which have a bubble pressure equal to the saturation pressure of R22 at a bubble temperature of 0 °C. The diagram was developed using the thermodynamic properties routines implementing the Carnahan-Starling-DeSantis equation of state, taken from the REFPROP package³.

First, it can be observed in Figure 4 that, as expected, the binary mixture of the components farthest apart in boiling points, R23/142b, shows the greatest nonlinearity. This binary mixture has two points of a 13.9 °C (25°F) glide, one of them occurring below the R22 isobar. Thus, the first part of the test plan was to perform tests with the binary mixture R23/142b starting with pure

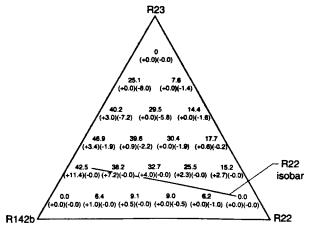


Figure 4 Temperature glide (°C) at $T_{bub} = 0$ °C for the mixture R23/22/142b

Figure 4 Glissement des températures à T_{bub}=0°C pour le mélange R23/22/142b

R142b until either efficiency began to drop off excessively or the R22 isobar was exceeded.

Also from Figure 4, we can observe that the best ternary linearity with a 13.9 °C (25 °F) glide occurs near the R22/142b binary line at approximately 60% R22. Technically, it would be most interesting to reach this point by following either a constant pressure or constant glide line from the R23/142b binary line. In practice, following such a line would be exceedingly difficult, and the decision was made to follow the easier test path of moving upward from approximately 50%/50% R22/142b in small increments of R23.

As a comment on the increased flexibility with ternary mixtures, one can follow the 13.9 °C (25°F) constant-glide line from the R23/142b binary line and observe that this glide may be achieved in the ternary region over a broad and continuously varying range of pressures, much of which is below the R22 isobar. In contrast, if one were restricted to binary combinations, there would be none with this glide using R22/142b, two with R23/142b (but only one below the R22 isobar) and two with R23/22 (both above the R22 isobar). The two binary 13.9 °C (25°F) glide points near the R23 apex would be expected to be critical or near critical in the condenser.

Test results and discussion

The primary goal of this project was to demonstrate improvement of two-phase linearity by the use of ternary mixtures. Hence, primary data analysis is to be directed at comparing evaporator temperature profiles; condenser instrumentation was inadequate to allow similar analysis of that heat exchanger. This said, the motivation for linearizing temperature glide is that it, theoretically, will improve efficiency. Therefore, it is useful to use an efficiency plot as a framework for analysis of test results.

The operating conditions of the performed tests and a summary of the test results are given in Table 1 of this paper. The coefficient of performance is presented as a function of evaporator refrigerant temperature glide in Figure 5. The pure refrigerants R22 and R142b are shown at the zero glide ordinate as tests 1 and 2. Pure R23 could not be tested because it is super-critical at room temperature. The difference in COP shown for the two pure refrigerants emphasizes the point that glide matching is not the only refrigerant property that affects cycle efficiency. It has previously been observed that, on this apparatus, lower volumetric capacity refrigerants such as R142b tend to show reduced COP as a result of compressor mechanical losses becoming a greater proportion of total capacity⁴. Individual refrigerant properties can also affect other efficiency-related areas

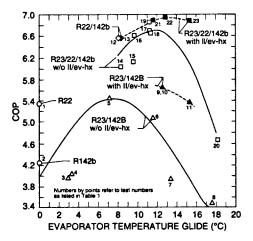


Figure 5 Coefficient of performance as a function of evaporator temperature glide

Figure 5 Rapport entre coefficient de performance et glissement des températures de l'évaporateur

Table I Measured data
Tableau 1 Données mesurées

Test	Composition R23/22/142b weight	Temperatures in evaporator		Temperatures in condenser		Refrig.		Evapor-		
		Water inlet/outlet (°C)	Refrigerant inlet/outlet (°C)	Water inlet/outlet (°C)	Refrigerant inlet/outlet (°C)	- at exp. valve inlet (°C)	pres- sor rev min ⁻¹	ator capa- city (kW)	СОР	II/ev-hx
1	0/100/0	26.6/12.9	12.9/13.2	47.2/27.7	62.9/31.2	30.3	501	4384	5.35	no
2	0/0/100	26.9/12.8	12.9/12.5	47.3/27.7	57.2/31.4	30.4	1269	3440	4.22	no
3	1.9/0/98.1	26.7/12.8	12.4/15.3	47.1/27.7	59.3/32.2	31.1	1226	3467	3.94	no
4	2.1/0/97.9	26.6/12.7	12.2/15.4	47.1/27.7	60.1/30.9	29.9	1195	3444	4.03	no
5	3.9/0/96.1	26.8/12.9	11.2/18.6	47.3/27.8	56.7/29.5	28.9	919	3417	5.42	no
6	7.9/0/92.1	26.7/12.8	8.3/20.0	47.2/27.7	66.1/28.2	27.9	848	3558	5.00	no
7	8.9/0/91.1	26.8/12.7	7.4/20.7	47.1/27.8	66.8/28.0	27.7	887	3250	3.94	no
8	13.9/0/86.1	26.7/12.8	4.7/22.3	47.3/27.7	73.3/28.1	27.8	850	3277	3.42	no
9	4.2/0/95.8	26.8/12.7	7.3/20.0	47.3/27.7	56.8/28.6	15.3	880	3499	5.62	yes
10	5.1/0/94.9	26.7/12.7	6.7/19.4	47.2/27.7	54.4/29.7	15.3	880	3482	5.56	yes
11	5.9/0/94.1	26.7/12.9	6.1/21.5	47.3/27.7	60.1/28.3	15.8	849	3555	5.28	yes
12	0/57.7/42.3	26.6/12.8	12.0/20.3	47.2/27.7	55.9/33.1	31.6	541	3329	6.52	no
13	0/57.1/42.9	26.7/12.9	11.9/20.6	47.3/27.7	56.1/31.6	15.1	540	3362	6.48	yes
14	0.6/53.6/45.8	26.6/12.6	11.7/20.2	47.2/27.7	56.8/31.2	30.2	523	3013	6.02	no
15	1.4/52.8/45.8	26.7/12.8	11.3/21.2	47.4/27.8	56.7/31.2	30.4	519	3098	6.09	no
16	2.0/53.1/44.9	26.6/12.9	11.2/21.2	47.1/27.8	56.1/31.3	30.4	520	3303	6.55	no
17	2.5/48.6/48.9	26.6/12.8	10.9/22.5	47.3/27.8	57.4/30.3	29.9	519	3262	6.62	no
18	3.6/54.4/42.0	26.7/12.9	10.2/22.0	47.1/27.7	57.5/30.1	29.8	504	3441	6.59	no
19	2.6/52.5/44.9	26.6/12.9	10.3/22.4	47.3/27.7	56.4/30.4	30.2	517	3370	6.79	no
20	10.9/47.3/41.8	26.6/12.6	5.8/24.3	47.2/27.7	60.4/28.8	28.9	846	5721	4.63	no
21	1.9/51.9/46.2	26.6/12.8	9.9/21.9	47.2/27.7	54.9/33.3	15.4	519	3256	6.82	yes
22	2.3/50.6/47.1	26.7/12.7	9.3/22.5	47.3/27.8	56.9/28.7	15.3	516	3338	6.87	yes
23	2.6/49.4/48.0	26.7/12.6	8.8/24.4	47.3/27.8	58.2/28.4	15.3	517	2270	6.82	yes

such as pressure drops and heat transfer coefficients. Throughout this discussion it must be remembered that every mixture test is performed with a different refrigerant. Effects due to glide matching versus other property changes can never be completely separated in an experimental study.

Referring to Figure 5, adding R23 to R142b improved the COP by 28% without and 33% with heat exchange between the liquid line and evaporator (tests 5 and 10 versus test 2). Adding R142b to R22 resulted in a 22% improvement in COP that did not show sensitivity to heat exchanger use (tests 12 and 13 versus test 1). Addition of R23 to the binary mixture R22/142b resulted in ternary COPs as much as 28% better than that of pure R22 (test 22 versus test 1). This peak COP matches that previously reported for the binary mixture R22/1141. The COP improvement reported by Mulroy et al. was slightly higher (32% versus 28% above) because subcooling was not employed for undergliding refrigerants in that test series. Use of the liquid-line/evaporator heat exchanger appears to slightly improve the COP for both the ternary mixture and the R23/142b binary mixture.

One interesting observation that can be made from Figure 5 is that a small amount of R23 seems to hurt performance, probably due to its low critical point. Tests 3 and 4, in which a small amount of R23 has been added to pure R142b, show lower efficiency than test 2 performed with pure R142b. With higher amounts of R23 efficiency improves as the benefits of glide matching are felt.

Before discussing experimental temperature profiles, it is useful to briefly discuss how water and refrigerant temperature profiles that are matching and linear against an entropy abscissa would appear when plotted against enthalpy and distance. Translation to an enthalpy axis would result in a small alteration, because entropy change is substantially enthalpy change divided by the absolute temperature, which exhibits a very small percentage change throughout the evaporator. Since a counter-flow evaporator was used and the water and refrigerant travelled the same distance during the heat exchange, the

temperature points will map directly over one another when going to a distance scale. Temperature profiles on the distance scale for tests 6, 12, 17 and 22 are shown in *Figure* 6.

On an enthalpy-distance coordinate diagram, the distance scale will distort the water temperature profile in accordance with the heat transfer equation, $q = UA\Delta T$, in which distance is proportional to A and U varies primarily with refrigerant quality and heat flux. No matter what the shape of the water temperature profile on the temperature-distance scale, going backwards will, by properties, map back to a straight line on a temperature-enthalpy diagram. If the refrigerant temperature-enthalpy profile is linear and matching that of water, it will appear on a temperature-distance scale as displaying a constant refrigerant-to-water temperature difference. The exercise of mapping temperature-distance plots to an abscissa that will give a linear water temperature profile (effectively mapping to temperatureenthalpy) has been carried out for the selected four tests in Figure 7, the abscissa of which has been dubbed pseudo-enthalpy. It is scaled in terms of equal total enthalpy units (i.e. mass flow × specific enthalpy change).

Tests 6 and 17 are good choices for comparing non-linear with linear profiles in that their glides are nearly equal: 11.8 °C (21.2 °F) and 11.6 °C (20.8 °F), respectively, approximately matching the evaporator—water glide of 13.9 °C (25 °F).

For ternary test 17 (R23/22/142b (2.5/48.6/48.9)), the mixture glide can be seen to be nearly linear and matching, as evidenced by a nearly uniform temperature difference between the refrigerant and water in Figure 6 and a linear refrigerant temperature profile in Figure 7. The concave shape of the two curves in Figure 6 is the result of greater heat transfer and hence greater water cooling on the right-hand side (water inlet and refrigerant outlet) of the curve resulting from the greater refrigerant-side heat transfer coefficient at high qualities, and the greater average refrigerant-to-water temperature difference resulting from this mixture being slightly undergliding.

The temperature plots for binary test 6 (R23/142b

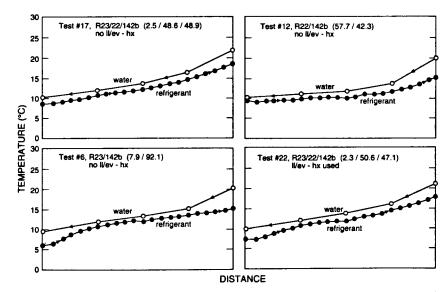


Figure 6 Evaporator temperature profiles on the distance scale for selected tests

Figure 6 Profils des températures de l'évaporateur sur un intervalle déterminé pour des essais spécifiques

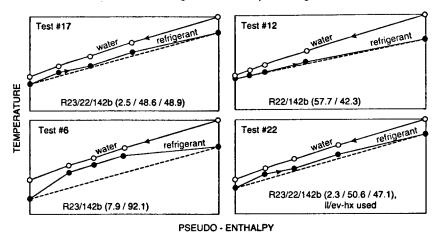


Figure 7 Evaporator temperature profiles remapped to force a linear temperature profile for the sensible heat transfer fluid

Figure 7 Profils des températures de l'évaporateur redessinés pour arriver à un profil des température linéaire des fluides caloporteurs sensibles

(7.9/92.1)) show a strong pinch point resulting from non-linearity for much of the midsection of the evaporator. Glide matching benefits cease once a coil begins to pinch. The only efficiency benefits expected from adding R23 are due to glide matching. Otherwise R23 addition would lower the COP due to its low critical temperature. Therefore, peak efficiency for R23/142b would be expected to occur with less R23 at a point where pinching has not yet occurred, as can be seen to be the case in Figure 6. Comparing with test 17, we have seen a demonstration that addition of the intermediate boiler, R22, will improve the linearity of the mixture R23/142b.

For the other binary mixture tested, R22/142b (57.7/42.3), test 12, the gradually increasing refrigerant—water temperature difference with pinching at the refrigerant inlet side indicates that linearity might be good (as can be seen to be the case in Figure 7), but that the temperature glide is much too small. The glide shown is nearly the highest possible with this binary mixture: hence this composition was chosen to constitute the base binary mixture to which R23 was added for ternary tests. Further tests demonstrated that, given a binary mixture of good linearity but insufficient glide, the glide may be increased without losing linearity by adding a third component outside the normal boiling point interval of the original constituents.

The final temperature profiles to be considered are those of the highest efficiency test, test 22 (R23/22/142b (2.3/50.6/47.1)). This ternary profile shows good linearity and glide matching. The liquid-line/evaporator heat exchanger used for this test results in a lower entry quality and, consequently, a less smooth curve than would be shown by the same mixture without such heat exchange. The benefit of this heat exchanger results from changed operating pressures and does not show in a temperature profile plot¹.

Conclusions

The two-phase, temperature-entropy linearity of a binary mixture was shown to be improved by the introduction of a third component of intermediate

normal boiling point. Generally speaking, the greater the difference in the normal boiling points of a binary's components the larger the temperature glide will be and the more non-linear the mixture temperature profile will be. However, it was demonstrated that the magnitude of the two-phase temperature glide of a linear binary mixture was increased without loss of linearity by addition of a third component outside the normal boiling point range of the original constituents.

The flexibility of ternary mixtures to provide a desired two-phase temperature glide over a broad range of component compositions and operating pressures was demonstrated.

The use of the liquid-line/evaporator heat exchange was shown to improve cycle COP for the refrigerant mixtures tested. With the combined effects of the glide matching and liquid-line/evaporator heat exchange, a 28% better COP was measured than that of pure R22.

Acknowledgements

The authors are indebted to the US Department of Energy for their continued sponsorship of this work and the other zeotropic mixtures work at NIST over the past decade; in particular to Mr John Ryan, Director of the Building Equipment Division, Conservation and Renewable Energy.

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